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HYDROTHERMAL SYNTHESIS OF LEUCITE AND ITS APPLICATION IN ENGINEERING CERAMICS

A. Balandis[1] and I. Sinkyavichene[1]

The conditions for producing tetragonal and cubic leucite from tetragonal analcime by hydrothermal ion exchange in an alkaline medium are identified. The process parameters are specified. A composite ceramic material based on cubic leucite is developed for the heating elements of plants for vacuum synthesis of pure inorganic compounds.

Leucite $KAlSi_2O_6$ belonging to the feldsparoid group is structurally close to the mineral analcime, i.e., hydrous sodium alumosilicate $Na[AlSi_2O_6] \cdot H_2O$. In most cases two varieties of leucite are used in engineering: of the tetragonal and the cubic syngony. Leucite of the cubic syngony is formed in oxide systems under firing at temperatures above 605°C [1]. As the ceramic mixtures cool, it changes into the tetragonal syngony [2, 3]. The modification of the crystal lattice parameters and the CLTE causes cracking in leucite-

[1] Kaunas Technological University, Kaunas, Lithuania.

based ceramic coatings that are extensively used for dental cement. It is established that dental cement of better quality can be obtained at temperatures of 800 – 1000°C if high-temperature cubic leucite is stabilized in firing by a Cs_2O additive [4 – 7].

We investigated the processes of producing cubic leucite by the ion-exchange method under hydrothermal conditions at temperatures below 200°C from presynthesized analcime and the possibility of using leucite in ceramics for electric heaters of vacuum synthesis plants.

TABLE 1

Composite	Duration, h	Al(OH)$_3$		Al$_2$O$_3$	
		molar ratio Na$_2$O : Al$_2$O$_3$: SiO$_2$	composition of products of synthesis	molar ratio Na$_2$O : Al$_2$O$_3$: SiO$_2$	composition of products of synthesis
1	0.5	2 : 1 : 5	Gibbsite	2 : 1 : 5	Cubic analcime
2	0.5	4 : 1 : 5	Tetragonal analcime	4 : 1 : 5	The same
3	0.5	2 : 1 : 6	Tetragonal analcime, gibbsite	2 : 1 : 6	″
4	0.5	4 : 1 : 6	Tetragonal analcime	4 : 1 : 6	″
5	1	2 : 1 : 6	Gibbsite	2 : 1 : 5	Cubic analcime, zeolite
6	1	4 : 1 : 5	Tetragonal analcime	4 : 1 : 5	Cubic analcime
7	1	2 : 1 : 5	The same	2 : 1 : 6	The same
8	1	4 : 1 : 6	″	4 : 1 : 6	″
9	3	2 : 1 : 5	Gibbsite	2 : 1 : 5	″
10	3	4 : 1 : 5	Tetragonal analcime	4 : 1 : 5	″
11	3	2 : 1 : 6	The same	2 : 1 : 6	″
12	3	4 : 1 : 6	″	4 : 1 : 6	″
13	8	2 : 1 : 5	Tetragonal analcime, gibbsite	2 : 1 : 5	″
14	8	4 : 1 : 5	Tetragonal analcime	4 : 1 : 5	″
15	8	2 : 1 : 6	The same	2 : 1 : 6	″
16	8	4 : 1 : 6	″	4 : 1 : 6	″
17	18	2 : 1 : 5	Tetragonal analcime, gibbsite	2 : 1 : 5	″
18	18	4 : 1 : 5	Tetragonal analcime	4 : 1 : 5	″
19	18	2 : 1 : 6	The same	2 : 1 : 6	″
20	18	4 : 1 : 6	″	4 : 1 : 6	″
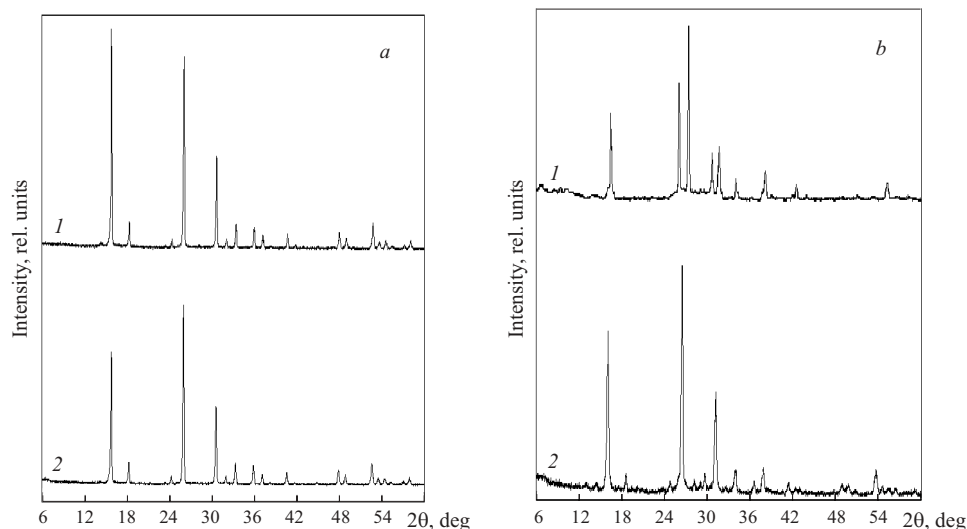
Fig. 1. X-ray diffraction curves: *a*) tetragonal (*1*) and cubic (*2*) analcime; *b*) tetragonal (*1*) and cubic (*2*) leucite.
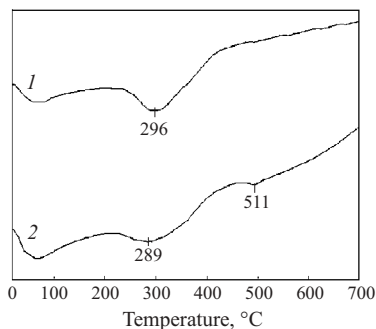
Fig. 2. Thermograms of tetragonal (*1*) and cubic (*2*) analcime.

The processes of the formation of analcime of different syngonoies (tetragonal and cubic) were investigated. Analcime both in natural and artificial conditions is formed in highly alkaline solutions [8]. The pH and temperature of the medium are the main conditions for the formation of analcime. Analysis of our experiments in the synthesis of analcime established that, apart from the specified factors, the compound in which the aluminum-bearing component is introduced is significant. Table 1 lists the conditions for the hydrothermal synthesis of analcime at a temperature of 180°C and the compositions of products obtained.

The composition of the products was identified by x-ray diffraction (DRON-6), differential-thermal (DuPont 990), and differential scanning (NETZSH Geratebau GmbH) analysis. It can be seen that the most significant factors in the process of analcime formation are the alkalinity of the medium and the type of the aluminum-bearing compound introduced into the initial mixture. With the $Na_2O : Al_2O_3$ ratio equal to 2 : 1 the formation of analcime in initial mixtures proceeds with difficulties and requires a lengthy isothermal

exposure. Mixtures in which aluminum hydroxide $Al(OH)_3$ is used as the aluminum-bearing component generate only tetragonal analcime, whereas mixtures containing amorphous Al_2O_3 as the aluminum-bearing component generate cubic-syngony analcime.

We investigated the process of formation of cubic analcime in suspensions stirred at temperatures of 130, 150, 180, and 200°C from initial mixtures using amorphous Al_2O_3 and increased quantities of SiO_2.

The experimental results corroborated that cubic analcime is formed at the temperature of synthesis of 150, 180, and 200°C and the upper limit of SiO_2 content in the initial mixtures is 7 moles. When this limit is exceeded, the formation of pure cubic analcime is significantly impeded.

Analcime and leucite minerals have similar crystal structures; therefore, they easily participate in mutual ion-exchanging reactions. To produce pure tetragonal and cubic leucite under hydrothermal conditions by ion-exchange reactions we used three-percent, six-percent, and saturated solutions of KCl, as well as presynthesized pure tetragonal and cubic analcime. The results of the experiments indicated that the reactions of synthesis of leucite by the ion-exchange method proceed intensely only in saturated KCl solution. Pure tetragonal leucite was formed at a temperature of 180°C after 0.5 h of isothermic exposure. Pure cubic leucite was obtained at 200°C after 24 h of isothermic exposure. In KCl solutions with a lower concentration the processes of formation of pure leucites by the ion-exchange method are less intense.
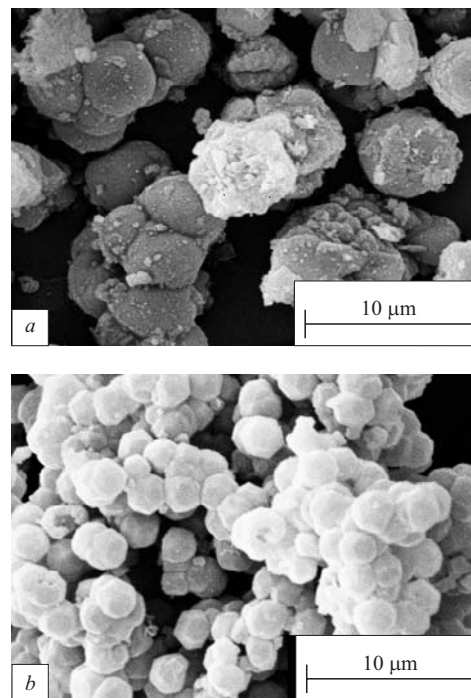
The x-ray diffraction curves of tetragonal and cubic analcime and leucite (Fig. 1) differ insignificantly due to a small difference (fractions of a nanometer) in the sizes of the crystal lattices. A more perceptible difference between the products of the synthesis of analcime of different syngonies is seen on DTA curves (Fig. 2) and IR spectra (Fig. 3).
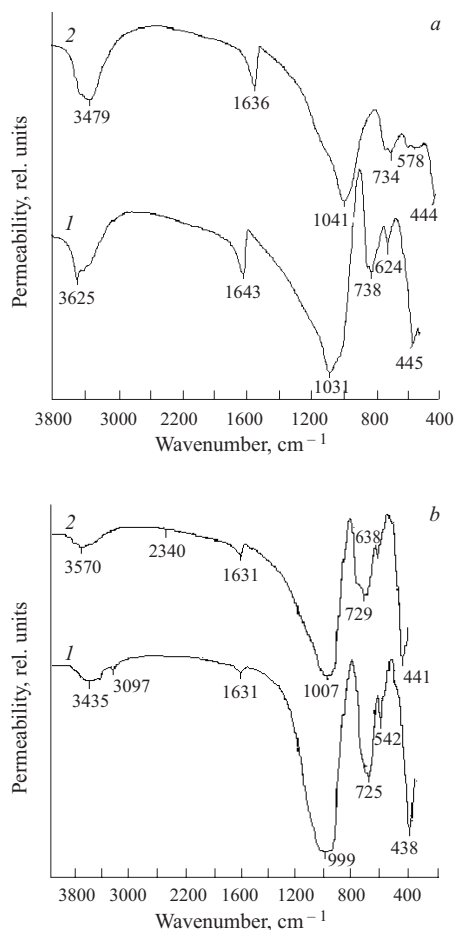
Fig. 3. IR spectra: *a*) tetragonal (*1*) and cubic (*2*) analcime; *b*) tetragonal (*1*) and cubic (*2*) leucite.

Fig. 4. Microscopic photos of tetragonal (*a*) and cubic (*b*) leucite.

The IR spectra of different syngonies of analcime and leucite exhibit a significant difference between the absorption spectra of these minerals in the range of valence ($1250 - 830$ cm^{-1}) and deformation ($800 - 400$ cm^{-1}) vibrations of the $Si - O$ and $Al - O$ bonds. The IR absorption spectra of the cubic syngony have an approximately half as narrow absorption band and their absorption maxima are shifted to the higher-frequency range and have fewer multiplicities of the maxima and lower intensities in the valence vibration range. All this indicates that the strength of the $Si - O$ and $Al - O$ bonds in analcime and leucite of the cubic syngony is higher and their structural elements (tetrahedra $[SiO_4]$ and $[AlO_4]$) are less deformed. A substantial difference in the form of the IR spectra of analcime and leucite of different crystalline syngonies facilitates their identification in the products of synthesis.

On the other hand, the affinity of the IR spectra of cubic leucite and cubic analcime indicates that the substitution of larger (by about 30%) K^+ ions for Na^+ ions in hydrothermal ion-exchange synthesis does not cause significant modifications in the crystal structure of analcime due to its zeolite type. The IR spectroscopy method established as well that

when cubic leucite is formed by the ion-exchange method in hydrothermal conditions, its structure contains insignificant quantities of adsorbed and crystallization water (which was not identified in thermal analysis). A similar phenomenon was also noted by other researchers for some feldsparoids, which earlier had been regarded as anhydrous minerals [9].

Leucite is characterized by its zeolite structure and a high CLTE. This creates prerequisites for its application not only in dental ceramic coatings but also as a component in composite ceramic materials. Other properties of leucite, such as the size and geometrical shape of its crystals, specific surface area, and density, are also important for producing homogeneous composite ceramics. The physical properties of cubic and tetragonal leucite synthesized from initial mixtures in which the molar ratio of $Na_2O : Al_2O_3 : SiO_2$ is equal to $3 : 1 : 7$ are listed in Table 2.

The method of stereo-electronic microscopy (Fig. 4) established that leucite crystals of cubic syngony are significantly smaller, have a more regular geometric shape, and a more extended specific surface area. The CLTE of cubic leu-

TABLE 2

Leucite*	Specific surface area, m^2/kg	Density, kg/m^3	CLTE, 10^{-6} K^{-1}	Refraction coefficient
Cubic	483.9	2376	12.40	1.5085 ± 0.002
Tetragonal	378.9	2469	8.42	1.4710 ± 0.002

* Ion-exchange conditions: cubic leucite) temperature 200°C, duration 24 h; tetragonal leucite) temperature 200°C, duration 0.5 h.

cite is approximately 1.5 times higher than that of tetragonal leucite; therefore, it is more suitable for ceramic composites direct contacting metals.

Composites based on cubic leucite were investigated for producing ceramic material to be used in electric heaters of plants for vacuum synthesis of pure inorganic compounds.

It is established that cubic leucite can be used to produce composite ceramics ensuring the stability of the heat flux transfer, as well as the required strength and constancy of the chemical composition in the temperature interval of $400 - 600°C$. Heating elements made of ceramic material based on cubic leucite are used in the plant for vacuum synthesis of pure inorganic compounds at the Physical Department of Kaunas Technological University.

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